NsG-5-59

UNIVERSITY OF MARYLAND

45p

N65-89038

~~X64 11531~~

~~Code 2A~~
Code 2d

NASA CR 55237

INSTITUTE FOR MOLECULAR PHYSICS

QUANTUM EFFECTS IN SMALL-ANGLE MOLECULAR BEAM SCATTERING

E. A. Mason, J. T. Vanderslice, and C.J.G. Raw

IMP-NASA-34

December 2, 1963

QUANTUM EFFECTS IN SMALL-ANGLE MOLECULAR BEAM SCATTERING*

E. A. Mason, J. T. Vanderslice, and C.J.G. Raw†

Institute for Molecular Physics, University of Maryland

College Park, Maryland

ABSTRACT

11531 over

Quantum-mechanical calculations of the differential cross section for the small-angle elastic scattering of heavy particles are carried out to establish more definitely the region of validity of the classical approximation. Four results are discussed: (1) The Massey-Mohr phase-shift formula corresponds to the Kennard small-angle scattering formula in the semiclassical limit. (2) The Schiff approximation for the cross section is exactly the same as the semiclassical approximation at small angles, for any central potential. (3) At very small angles the semiclassical limit for the differential cross section varies as exp $(-c\theta^2)$, where c is a function of velocity for which explicit expressions are given. (4) The first quantum deviation from the classical limit, which is proportional to $\hbar^2$, can be combined with the preceding result to give a reasonable representation of the

* Supported in part by the National Aeronautics and Space Administration (Grant NsG-5-59).

† Permanent address: Department of Chemistry, Saint Louis University, St. Louis, Missouri.

11531

differential cross section over the entire range of small angles for which quantum deviations are appreciable. Detailed calculations for some specific systems are made, and it is shown that Wu's misgivings over the classical interpretation of the experimental results of Amdur and coworkers are unjustified.

AUTHOR

I. INTRODUCTION

It is well known that the classical treatment of heavy particle scattering always fails at sufficiently small scattering angles, so that measurements of molecular beam scattering cannot be analyzed in terms of classical mechanics if the observations include contributions from these small angles. For instance, Wu[1] has questioned the classical analysis of the scattering results for the He-He system, particularly the results of Amdur and Harkness,[2] which extend down to angles of the order of 10^{-3}rad. The usual criteria[3] for the applicability of classical mechanics are sufficient, rather than necessary, conditions, however, and may well be too stringent. More quantitative criteria for the validity of the classical approximation are therefore desirable. Knowledge of the details of the scattering in the quantum region would also be desirable, since this region is experimentally easily accessible with low-energy molecular beams. In view of the current interest in molecular beam scattering studies, both in the thermal and high-energy ranges, it is of interest to investigate these questions theoretically.

The purpose of this paper is to carry through the quantum calculations of the differential cross section $\sigma(\theta)$ for small-angle elastic scattering, and to use these calculations to establish more definitely the region of validity of the classical approximation. Particular attention is paid to the experimental results of Amdur and coworkers.

The usual criterion for the applicability of classical mechanics is that the uncertainty in the momentum of a colliding system be small compared to the momentum transferred in the collision. (Another criterion, that the de Broglie wavelength be small compared to the range of the scattering field, is usually well satisfied.) The momentum uncertainty is usually taken to be about $\hbar/(2r_o)$, where r_o is the range of the scattering field (often taken to be the classical distance of closest approach), and the momentum transferred in small-angle scattering is approximately $\mu v\theta$, where μ is the reduced mass, v the relative velocity, and θ the relative deflection angle.[4,5] The criterion thus becomes $\hbar/(2\mu v r_o\theta) \ll 1$. For Amdur and Harkness' He-He results, this ratio varied from 0.18 to 0.12, not extremely small compared to unity, but hardly large enough to be certain that the classical approximation is invalid.[6] Amdur[6] has cited independent indirect evidence indicating that the classical approximation is probably valid for analyzing his measurements, but the important question of a more quantitative criterion of validity remains open.

A rough quantitative criterion for classical scattering was given long ago by Massey and Mohr[7a] for the case of rigid spheres of diameter r_o, which was that the classical result was valid for angles larger than a "critical" angle θ_c, whose value is approximately

$$\theta_c \approx \pi/(kr_o) = \pi\hbar/(\mu v r_o), \qquad (1)$$

where $k = \mu v/\hbar$ is the wave number of the relative momentum. This result can be extended to other than rigid spheres by interpreting r_o as the classical distance of closest approach for scattering through the angle θ_c.[7b] When this is done, and the results compared with the few relevant experimental measurements involving beams of thermal energies, it appears that the classical values may hold accurately right down to θ_c, and begin to deviate only for smaller angles.[8,9] There is no special reason to think the situation different for high energy beams. In terms of the critical angle, the previous sufficient condition for classical scattering becomes $\theta \gg \theta_c/2\pi$, which indeed seems too stringent a criterion. Our detailed calculations confirm these conclusions, and also yield an explicit general formula for $\sigma(\theta)$ in the small-angle quantum region. This can be combined with an expression for the initial deviations from the classical $\sigma(\theta)$, so that the whole angular region from $\theta = 0$ to the classical limit is fairly well covered.

II. GENERAL FORMULAS

The general problem is to find solutions of the Schroedinger wave equation for a particle of mass μ and wave number k, moving in a scattering potential field V(r),[10]

$$\nabla^2\psi + (k^2 - U)\psi = 0, \tag{2}$$

where $U = 2\mu V/\hbar^2$. The solution must have the asymptotic form

$$\psi \longrightarrow \exp(ikz) + r^{-1} f(\theta)\exp(ikr), \tag{3}$$

where the z-axis is chosen along the direction of incidence of the beam. The quantity $f(\theta)$ is the scattered amplitude, which determines the differential cross section according to the formula

$$\sigma(\theta) = |f(\theta)|^2, \tag{4}$$

which is valid when the beam and scattering particles are distinguishable. If the colliding particles are indistinguishable, the wave function must satisfy certain symmetry conditions, and Eq.(4) must be modified because the scattered beam particles cannot be distinguished from the recoil scattering particles.[7,11] However, all the experiments to which we shall refer are concerned with particles which are in practice distinguishable, and so these points do not concern us.[12]

There are two usual methods of solving this problem: the method of partial waves,[7,10,11] and an integral equation method[4,13] which leads to the infinite Born series.

A. Phase-Shift Series

The method of partial waves gives the scattered amplitude in terms of the phase shifts δ_ℓ for the partial waves of the asymptotic solution,[7,10,11]

$$f(\theta) = (2ik)^{-1} \sum_{\ell=0}^{\infty} (2\ell + 1) \left[\exp(2i\delta_\ell) - 1\right] P_\ell(\cos\theta), \tag{5}$$

where ℓ is the angular momentum quantum number and the $P_\ell(\cos\theta)$ are Legendre polynomials. A quantity often determined experimentally is the "total" scattering cross section,

$$S(\theta_o) = 2\pi \int_{\theta_o}^{\pi} \sigma(\theta) \sin\theta \, d\theta, \tag{6}$$

where θ_o is the angular aperture (resolving power) of the apparatus. For $\theta_o = 0$, Eq.(6) can be integrated to give the true total cross section,[7,10,11]

$$S(0) = (4\pi/k^2) \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2\delta_\ell . \tag{7}$$

At $\theta = 0$ we have $P_\ell(1) = 1$, and comparison of Eqs. (5) and (7) gives a general relation between S(0) and the imaginary part of f(0),[11]

$$S(0) = (4\pi/k) \operatorname{Im}\left[f(0)\right]. \tag{8}$$

An approximate formula for S(0) in terms of f(0) can be obtained by substituting Eq. (5) back into Eq. (4) and writing

$$\sigma(\theta) = (4k^2)^{-1} \left| \sum_\ell (2\ell + 1)(2 \sin^2\delta_\ell) P_\ell(\cos\theta) \right|^2$$
$$+ (4k^2)^{-1} \left| \sum_\ell (2\ell + 1)(\sin 2\delta_\ell) P_\ell(\cos\theta) \right|^2 . \tag{9}$$

Under some circumstances it is permissable to neglect the second summation on the right compared to the first summation, in which case we obtain the simple approximation[7]

$$S(0) \approx (4\pi/k)\left[\sigma(0)\right]^{\frac{1}{2}} = (4\pi/k)\left|f(0)\right|. \tag{10}$$

The phase shifts δ_ℓ are to be calculated by integration (usually numerical) of the radial wave equation. Since such integration is very laborious except for a few simple forms of V(r), approximations are usually introduced in the calculation of the δ_ℓ.

B. Infinite Born Series

A formal solution of the wave equation (2) with the correct asymptotic form can be obtained in the form of an integral equation[4]

$$\psi \longrightarrow \exp(ikz) + (4\pi r)^{-1}\exp(ikr)\int \exp\left[-ik(\underset{\sim}{n}\cdot\underset{\sim}{r}')\right]U(r')\psi(\underset{\sim}{r}')\,d\tau', \tag{11}$$

where $\underset{\sim}{n}$ is a unit vector in the direction of $\underset{\sim}{r}$, and $d\tau' = dx'dy'dz'$. Equation (11) can be solved by iteration, so that $f(\theta)$ is obtained as the infinite Born series

$$f(\theta) = \sum_{n=1}^{\infty}\int\cdots\int \exp\left[-ik(\underset{\sim}{n}\cdot\underset{\sim}{r}_n)\right]G(\underset{\sim}{r}_n-\underset{\sim}{r}_{n-1})\cdots G(\underset{\sim}{r}_2-\underset{\sim}{r}_1)\times$$

$$\times\, U(r_n)\cdots U(r_1)\exp(ikz_1)\,d\tau_1\cdots d\tau_n, \tag{12}$$

where

$$G(\underset{\sim}{\rho}) = -(4\pi\rho)^{-1}\exp(ik\rho). \tag{13}$$

The first term of the series yields the usual first Born approximation; higher terms are very laborious to calculate unless approximations are made.[13]

III. APPROXIMATION METHODS

A. Semiclassical Approximation

In the summation over phase shifts of Eqs.(5), (7), and (9), a large number of terms are required in all cases except the scattering of very light particles at very low energies (corresponding to temperatures far below room temperature). Furthermore, it is the phase shifts for large ℓ which are the most important. It is therefore a good approximation to replace the summations over ℓ by integrations over $d\ell$, provided of course that one can also approximate both P_ℓ and δ_ℓ as continuous functions of ℓ. These three approximations can all be made, and together constitute what is called the semiclassical treatment of scattering. A particularly thorough and lucid discussion of the semiclassical method has been given by Ford and Wheeler.[14]

The P_ℓ are represented by two asymptotic formulas valid for large ℓ, one valid for small angles $(\sin\theta < 1/\ell)$,[14,15]

$$P_\ell(\cos\theta) \approx (\cos\theta)^\ell \, J_0\left[(\ell + \tfrac{1}{2})\theta\right], \tag{14}$$

where J_0 is the Bessel function of order zero, and the other valid for large angles $(\sin\theta > 1/\ell)$,[14,16]

$$P_\ell(\cos\theta) \approx \left(\frac{2}{\pi\ell\sin\theta}\right)^{\frac{1}{2}} \left[\left(1 - \frac{1}{4\ell} + \cdots\right)\sin\phi - \frac{1}{8\ell}\cot\theta\cos\phi + \cdots\right], \tag{15}$$

where

$$\phi = (\ell + \tfrac{1}{2})\theta + \tfrac{1}{4}\pi\,. \tag{16}$$

The δ_ℓ are represented by the JWKB approximation, with the Langer modification of replacing $\ell(\ell+1)$ by $(\ell+\frac{1}{2})^2$. Letting $b = (\ell+\frac{1}{2})/k$, we can write this approximation as[4,14]

$$\delta_\ell = \delta(b) \approx k\int_{r_o}^{\infty}\left[1-(b/r)^2 - (U/k^2)\right]^{\frac{1}{2}} dr - k\int_{b}^{\infty}\left[1-(b/r)^2\right]^{\frac{1}{2}} dr, \tag{17}$$

where the lower limit of each integral is the zero of its integrand. The limit r_o is the analogue of the classical turning point of the motion (the distance of closest approach in scattering), and the limit b is the analogue of the classical impact parameter. Direct differentiation of Eq. (17) leads to the semiclassical relation between the phase shifts and the classical deflection angle,[4,11]

$$\theta(b) = (2/k)(d\delta/db) = 2(d\delta_\ell/d\ell)\,. \tag{18}$$

For large ℓ a further simplification of Eq. (17) is possible, because r_o is then also large and approximately equal to b. The value of U(r) is therefore small throughout the range of integration, and the first integrand can then be expanded into a binomial series and the two integrals combined. The result is

$$\delta(b) \approx -\ (k/2)\int_b^\infty (U/k^2)\left[1-(b/r)^2\right]^{-\frac{1}{2}} dr. \tag{19}$$

This approximation was first proposed by Massey and Mohr[7b] (see also Landau and Lifshitz[11]). The classical analogue of the Massey-Mohr approximation for the phase shifts is the Kennard[17] approximation for the deflection angle in small-angle classical scattering, which for $r_o \approx b$ can be written as

$$\theta = (b/E)\int_b^\infty \left[V(b)-V(r)\right]\left[1-(b/r)^2\right]^{-3/2} dr, \tag{20}$$

where $E = \mu v^2/2$. It is easily verified that Eqs.(19) and(20) are related by differentiation according to Eq.(18).

Combining these results, we can write the semiclassical approximation for the total scattering cross section as

$$S(0) = 8\pi\int_o^\infty \left[\sin^2\delta(b)\right] bdb, \tag{21}$$

and the scattered amplitude as

$$f(\theta) = -ik\int_o^\infty \exp\left[2i\delta(b)\right] P(b,\theta)\, bdb, \tag{22}$$

where the term $\Sigma(2\ell+1)P_\ell$ from Eq.(5) has been set equal to zero.[11] This is valid except for $\theta = 0$. The differential cross section can be written as

$$\sigma(\theta) = 4k^2\left|\int_o^\infty \left[\sin^2\delta(b)\right] P(b,\theta)\, bdb\right|^2 + \\ + k^2\left|\int_o^\infty \left[\sin 2\delta(b)\right] P(b,\theta)\, bdb\right|^2, \tag{23}$$

which is valid even at $\theta = 0$. In Eqs.(22) and (23), $P(b,\theta)$ is given by one of the following two expressions, depending on whether θ is smaller or larger than $(kb)^{-1}$:

$$P(b,\theta) \approx J_0(kb\theta) \qquad \text{for} \qquad \theta < (kb)^{-1}, \tag{24}$$

$$P(b,\theta) \approx (\tfrac{1}{2}\pi kb \sin\theta)^{-\frac{1}{2}}\Big[\sin\phi - \\ -(8kb)^{-1}(\cot\theta\,\cos\phi + 2\sin\phi) + \cdots\Big] \text{ for } \theta > (kb)^{-1}, \tag{25}$$

where $\phi = (kb\theta + \frac{1}{4}\pi)$ as in Eq.(16). In Eq.(24) we have limited ourselves only slightly by discarding the $(\cos\theta)^{\ell}$ factor which appeared in Eq.(14). The expression for $\delta(b)$ is given by Eq.(17) for all θ, and by Eq.(19) for small θ. It should be mentioned that θ can be small compared to unity but nevertheless considerably larger than $(kb)^{-1}$.

B. Method of Stationary Phase and the Classical Limit

The method of stationary phase has been reviewed by Eckart[18] and by Erdélyi,[19] and we merely quote the results here since we need to make use of the method. Consider the integral

$$I = \int_0^\infty g(t)\exp\Big[i\Phi(t)\Big]dt. \tag{26}$$

If there is a point τ where Φ is stationary with respect to t, i.e. where $\Phi'(t) = 0$, then most of the contribution to the integral comes from the vicinity of this stationary point, since elsewhere the exponential factor oscillates rapidly as Φ varies with t and the oscillations effectively integrate to zero. The integral can then be evaluated by expanding Φ as a Taylor series about τ and integrating to obtain

$$I = \left[2\pi/\Phi''(\tau)\right]^{\frac{1}{2}} g(\tau)\exp\left[i\Phi(\tau)+(i\pi/4)\right]+\cdots \quad . \tag{27}$$

When the exponential in Eq.(26) has a real instead of an imaginary argument, this approximation procedure is called Laplace's method.[20] The remainder in the approximation can be estimated by integration by parts.[18,19]

The classical limit of $\sigma(\theta)$ is obtained by applying the method of stationary phase to the semiclassical integral for $f(\theta)$ given in Eq.(22), with just the first term from Eq.(25) used for $P(b,\theta)$:

$$f(\theta) = -k^{\frac{1}{2}}(2\pi \sin\theta)^{-\frac{1}{2}}\int_0^\infty \left[\exp(i\Phi_+) - \exp(i\Phi_-)\right] b^{\frac{1}{2}}\, db, \tag{28}$$

where $\Phi_\pm = 2\delta(b) \pm \phi$. Depending on the sign of δ, one of the exponents has a stationary point and the other one does not, so that most of the contribution to the integral comes from the stationary point of only <u>one</u> of the exponents. To this approximation we can then write

$$f_{c\ell}(\theta) \approx \mp (kb/\sin\theta)^{\frac{1}{2}} \left|2d^2\delta/db^2\right|^{-\frac{1}{2}} \exp\left[(i\Phi_\pm)+(i\pi/4)\right] . \tag{29}$$

Taking the absolute value and making use of Eq.(18), we obtain

$$\sigma_{c\ell}(\theta) = \left|f_{c\ell}(\theta)\right|^2 = (b/\sin\theta)\left|d\theta/db\right|^{-1}, \tag{30}$$

which is exactly the classical result. Our reason for outlining this well-known derivation here is to call attention to the things that have been dropped in obtaining the classical result, and which must presumably be included to obtain at least a first quantum correction. These are: higher terms in the asymptotic expansion of $P(b,\theta)$ in Eq.(25), and remainders in the stationary phase approximation (including that one of the Φ exponents which did not have a stationary point). The use of the JWKB approximation for the phases is expected to be quite accurate.[7,21] The replacement of the summation over ℓ by an integration should also be accurate, and can be checked by taking higher terms in the Euler-Maclaurin summation formula.[22]

C. Schiff Approximation

The Schiff approximation is obtained by summing the infinite Born series after approximating each term by the method of stationary phase.[13] For axially symmetric scattering potentials Schiff's approximation for the total cross section can be written as

$$S(0) = 4\pi\int_0^\infty \left[1-\cos 2\zeta\ (b)\right] bdb, \tag{31}$$

where

$$\zeta(b) = (4k)^{-1} \int_{-\infty}^{\infty} U(b,z)\,dz, \tag{32}$$

and for the scattered amplitude at small scattering angles as

$$f(\theta) = ik\int_0^\infty \left[1-\exp(-2i\zeta)\right] J_0(qb)\,bdb, \tag{33}$$

where $q = 2k\sin(\theta/2) \approx k\theta$ for small angles. At small deflection angles $z^2 = r^2 - b^2$ and $dz = \left[1-(b/r)^2\right]^{-\frac{1}{2}} dr$, so that Eq.(32) becomes

$$\zeta(b) = (2k)^{-1}\int_b^\infty U(b,z)\,dz = (1/2)\int_0^\infty (U/k)\left[1-(b/r)^2\right]^{-\frac{1}{2}} dr. \qquad (34)$$

On comparing this with the small-angle approximation for the phase shifts given in Eq.(19) (the Massey-Mohr approximation), we see that $\zeta(b)$ is just the negative of $\delta(b)$. Thus Eq.(31) for the total cross section corresponds to the semiclassical expression given in Eq.(21)(since $\cos 2\zeta = 1-2\sin^2\zeta$), and Eq.(33) for the scattered amplitude corresponds (except at $\theta=0$) to the semiclassical Eq.(22) with P replaced by J_0 according to Eq.(24). At small angles, therefore, the Schiff approximation corresponds exactly to the semiclassical approximation. It is gratifying that these two different approximation procedures yield the same results. Their equivalence seems to have escaped notice for some time, however, and only recently has it been noticed[23] that the two procedures give the same result for the total cross section for inverse power potentials. We see from the foregoing that the equivalence is more general, and holds for both the differential and total cross sections for any central potential.

IV. CALCULATIONS

A. General Remarks

To get an accurate expression for $\sigma(\theta)$ we must first assume an algebraic form for V(r), find $\delta(b)$ from Eq.(19) by integration, and then evaluate $\sigma(\theta)$ from Eq.(22) or Eq.(23) by another integration. We shall carry through such calculations in detail in this section for some simple forms of $V(r)$, particularly inverse power repulsions or attractions for which most of the integrations can be carried out in closed form, but first we wish to show that very general approximate results can be obtained without any assumptions about $V(r)$ other than that it is monatonic. These results give $\sigma(\theta)$ as an explicit function of θ and $S(0)$, and to a rough approximation are independent of the form of $V(r)$. We consider two cases - very small angles where the deviations from classical behavior are large, and larger angles where the results are almost classical.

For very small angles we start with Eq. (23) for $\sigma(\theta)$. Since $\delta(b)$ is large and varies rapidly with b, the value of $\sin^2\delta$ oscillates rapidly between 0 and 1 out to some large value of b, and then rapidly decays to 0 at still larger b. Similarly, the value of $\sin 2\delta$ oscillates between -1 and +1 out to a large value of b, and then decays to 0. A rough approximation can therefore be obtained by replacing $\sin^2\delta$ and $\sin 2\delta$ by their average values of 1/2 and 0, respectively, out to $b=b_o$, and setting them equal to zero for $b>b_o$. This is a crude random-phase approximation. Substituting these approximations into Eq. (23) together with the series expression for J_o,

$$J_o(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 4^2} - \frac{x^6}{2^2 4^2 6^2} + \cdots , \tag{35}$$

we can integrate term by term. The first few terms of the resulting series are nearly the same as those for the series expansion of an exponential function, so that an exponential can be substituted for the series expansion with little error at very small angles. This substitution is not basic, but merely serves to consolidate the form of the final result. The vaguely specified parameter b_o is then eliminated in favor of S(0) by noting from Eq.(21) that $S(0)=2\pi b_o^2$ in this approximation, and the final result can be written as

$$\sigma(\theta) \approx \sigma(0) \exp\left[-S(0) k^2 \theta^2/(8\pi)\right], \tag{36}$$

with $\sigma(0)$ given approximately in terms of S(0) by Eq.(10).

This derivation takes inadequate account of the behavior of $\sin^2\delta$ and $\sin 2\delta$, especially for "soft" potentials, but the only effect of a more careful calculation is to introduce one constant into the exponent of Eq.(36) and another constant into Eq.(10). These constants are of order unity and depend on the form assumed for V(r), but the dependence of $\sigma(\theta)$ on θ is not affected by this refinement. The expression (36) for $\sigma(\theta)$ is not entirely new; a variation of $\sigma(\theta)$ approximately as $\exp(-\theta^2)$ has been pointed out previously in connection with scattering by the long-range r^{-6} London potential (van der Waals potential).[9a,24]

For larger angles we can obtain from the foregoing analysis a rough lower limit for the critical angle, θ_c, above which the classical results are valid. We have used the small-angle approximation $P \approx J_o$ out to an impact parameter of b_o, and obtained quantum results valid for $\theta < (kb_o)^{-1}$ according to Eq.(24). For somewhat larger angles, we may expect that Eq.(25) for P is valid, and the first term of Eq.(25) yields the classical result. Hence θ_c must surely be greater than $(kb_o)^{-1}$, or

$$\theta_c > k^{-1}\left[2\pi/S(0)\right]^{\frac{1}{2}} . \tag{37}$$

This lower limit is smaller than the Massey-Mohr value of θ_c given in Eq.(1) by a factor of π (since $r_o \approx b_o$ for small deflection angles).

For larger angles we can also investigate the effect of keeping higher terms in the approximation for P given by Eq.(25), and thereby get some indication of the initial deviations from the classical result. Substituting Eq.(25) into Eq.(22) we obtain

$$\begin{aligned} f(\theta) = & -k^{\frac{1}{2}}(2\pi \sin\theta)^{-\frac{1}{2}}\int_0^\infty \left[1-(4kb)^{-1}+\cdots+i(8kb)^{-1}\cot\theta+\cdots\right] \times \\ & \times \exp(i\Phi_+)\, b^{\frac{1}{2}} db \\ & + k^{\frac{1}{2}}(2\pi \sin\theta)^{\frac{1}{2}}\int_0^\infty \left[1-(4kb)^{-1}+\cdots - i(8kb)^{-1}\cot\theta+\cdots\right] \times \\ & \times \exp(i\Phi_-)\, b^{\frac{1}{2}} db, \end{aligned} \tag{38}$$

which gives, by the stationary phase approximation,

$$\begin{aligned} f(\theta) \approx \mp & (kb/\sin\theta)^{\frac{1}{2}} \left|2d^2\delta/db^2\right|^{-\frac{1}{2}} \exp\left[(i\Phi_\pm)+(i\pi/4)\right] \times \\ & \times\left[1-(4kb)^{-1}+\cdots\pm i(8kb)^{-1}\cot\theta+\cdots\right]. \end{aligned} \tag{39}$$

From this we obtain, on writing $\cot\theta = \theta^{-1} + \cdots$,

$$\sigma(\theta) \approx \sigma_{c\ell}(\theta)\left[1-(2kb)^{-1} + \cdots + (8kb\theta)^{-2} + \cdots\right]. \tag{40}$$

To obtain an estimate of magnitudes, let us rewrite this in terms of the Massey-Mohr expression for the critical angle, $\theta_c \approx \pi/(kb)$:

$$\sigma(\theta_c) \approx \sigma_{c\ell}(\theta_c)\left[1-(\theta_c/2\pi) + \cdots + (1/8\pi)^2 + \cdots\right]. \tag{41}$$

Since θ_c is usually less than 0.1 rad, the first correction term will usually amount to less than 2%. The second correction term contributes less than 0.2% at this angle. We therefore conclude that the major deviations from the classical expression at angles less than θ_c are not due solely to the approximation for P given in Eq. (25). This leaves the stationary phase approximation to be blamed.

To obtain more accurate results for $\sigma(\theta)$ we must now assume an analytic form for the potential.

B. Small-Angle Quantum Formulas

We first assume a potential of the form

$$V(r) = \pm K/r^s, \tag{42}$$

where K and s are positive constants. Inserting this into Eq. (19) and integrating, we obtain the Massey-Mohr approximation for the phase shifts[7b,11]

$$\delta(b) = \mp \mu K C_s\left[(s-1)\hbar^2 k b^{s-1}\right]^{-1} = -\tfrac{1}{2}kb\left[U(b)/k^2\right]\left[C_s/(s-1)\right], \tag{43}$$

where

$$C_s = \pi^{\frac{1}{2}} \Gamma(\tfrac{1}{2}s + \tfrac{1}{2}) / \Gamma(\tfrac{1}{2}s) . \qquad (44)$$

Let us first evaluate S(0) by substituting (43) back into the semiclassical Eq.(21) and integrating. If the integration variable is changed from b to δ and an integration by parts performed, the remaining integral is a known form,[25] and the final result is

$$S(0) = F(s)\left[K/(\hbar v)\right]^{2/(s-1)}, \qquad (45)$$

where

$$F(s) = \pi^2\left(\frac{2C_s}{s-1}\right)^{2/(s-1)}\left[\Gamma\left(\frac{2}{s-1}\right)\sin\left(\frac{\pi}{s-1}\right)\right]^{-1}, \quad s>2. \qquad (46)$$

A simpler approximate integration has been given by Massey and Mohr,[7b] who replaced $\sin^2\delta$ by its average value of 1/2 out to $b = b^*$, where b^* is that value of b for which $\delta(b^*) = 1/2$, and replaced $\sin^2\delta$ by δ^2 for $b>b^*$. This random-phase approximation is an improvement over our previous rough approximation of setting $\sin^2\delta$ equal to zero for $b>b_0$, and yields the result

$$F(s) \approx \pi\left(\frac{2s-3}{s-2}\right)\left(\frac{2C_s}{s-1}\right)^{2/(s-1)}, \quad s>2, \qquad (47)$$

which is equal to the more accurate result of Eq.(46) for $s = \infty$ (rigid spheres), and is 5 to 7% smaller for s between 10 and 3 (7% smaller at $s = 6$).[23]

It is also easy to evaluate $\sigma(0)$ by substituting (43) into the semiclassical Eq.(23) and putting $P(b,0) = 1$. The first term can be written in terms of S(0) and gives the previous approximate Eq. (10). The second term, involving $\sin 2\delta$, was set equal to zero by Massey and Mohr[7a] in their treatment of rigid spheres. This is correct for rigid spheres but produces appreciable error for "soft" potentials with finite values of s. The integral in the second term is a known form, and the result is

$$\sigma(0) = \left[\frac{kS(0)}{4\pi}\right]^2 \left[1 + \tan^2\left(\frac{\pi}{s-1}\right)\right], \qquad s>3, \tag{48}$$

so that the second term becomes equal to the first term for $s = 5$ and dominates the first term for $s<5$. Using the simpler Massey-Mohr approximation of taking $\sin 2\delta$ equal to zero out to b^*, and equal to 2δ for $b>b^*$, we obtain an expression similar to Eq. (48), but with the Massey-Mohr random-phase approximation for S(0) as given by Eq. (47), and with the tangent term replaced as follows:

$$\tan\left[\pi/(s-1)\right] \longrightarrow \left[4/(s-3)\right]\left[(s-2)/(2s-3)\right]. \tag{49}$$

For this expression the second term dominates the first term for $s > 4.69$.

To evaluate $\sigma(\theta)$ we substitute (43) into (23), replace P by J_0 according to (24), write J_0 as the series given in Eq. (35), and integrate term by term to obtain

$$\begin{aligned}\sigma(\theta) = {} & \left[\frac{kS(0)}{4\pi}\right]^2 \left[1 - f_1(s)\left(\frac{k^2 S(0)\theta^2}{16\pi}\right) + \cdots\right]^2 \\ & + \left[\frac{kS(0)}{4\pi}\tan\left(\frac{\pi}{s-1}\right)\right]^2 \left[1 - f_2(s)\left(\frac{k^2 S(0)\theta^2}{16\pi}\right) + \cdots\right]^2,\end{aligned} \tag{50}$$

where

$$f_1(s) = 2\left[\Gamma\left(\frac{2}{s-1}\right)\ \sin\left(\frac{\pi}{s-1}\right)\right]^2\left[\pi\Gamma\left(\frac{4}{s-1}\right)\ \sin\ \left(\frac{2\pi}{s-1}\right)\right]^{-1},\ s>3, \tag{51}$$

$$f_2(s) = f_1(s)\left[\tan\ \left(\frac{2\pi}{s-1}\right)\right]\left[\tan\left(\frac{\pi}{s-1}\right)\right]^{-1},\quad s>5. \tag{52}$$

Equation (50) can be approximately summed for small values of θ, and put into the more compact exponential form,

$$\sigma(\theta) = \left[\frac{kS(0)}{4\pi}\right]^2\left[1+\tan^2\left(\frac{\pi}{s-1}\right)\right]\exp\left[-f(s)k^2S(0)\theta^2/(8\pi)\right], \tag{53}$$

where

$$f(s) = \left[\Gamma\left(\frac{2}{s-1}\right)\right]^2\left[2\pi\Gamma\left(\frac{4}{s-1}\right)\right]^{-1}\tan\left(\frac{2\pi}{s-1}\right),\quad s>5. \tag{54}$$

The value of $f(s)$ is unity for $s=\infty$ (rigid spheres) and not too far from unity for values of s as low as 6. Equation (53) sums the series in (50) exactly to the number of terms written; higher terms are of the correct form, but their numerical coefficients begin to deviate from the correct values. Equation (53) thus becomes inaccurate when the value of the exponent becomes larger than about 1/2. If we put this criterion in terms of the critical angle given in Eq. (1), taking $r_o = \left[S(0)/2\pi\right]^{\frac{1}{2}}$, we find Eq. (53) to be accurate for angles

$$\theta < \left[\pi^2 f(s)/2\right]^{-\frac{1}{2}}\ \theta_c\ . \tag{55}$$

This corresponds to $\theta<0.45\theta_c$ for $s=\infty$ and $\theta<0.31\theta_c$ for $s=6$.

If the integrations leading to Eq. (53) are carried out by the Massey-Mohr random-phase approximation, results of the same form are obtained, but with the tangent term in front of the exponential replaced as in (49), and with f(s) in the exponent given by

$$f(s) \approx 4\left(\frac{s-2}{s-3}\right)\left(\frac{s-2}{2s-3}\right)^2\left[1+\left(\frac{4}{s-5}\right)\left(\frac{4}{2s-3}\right)\right]\left[1+\left(\frac{4}{s-3}\right)^2\left(\frac{s-2}{2s-3}\right)^2\right]^{-1}. \tag{56}$$

The Massey-Mohr approximation agrees exactly with the more accurate calculation for $s = \infty$; for $s = 11$ the coefficient in front of the exponential is smaller by a factor of 0.955 and f(s) is smaller by a factor of 0.992; for $s = 6$ the coefficient is smaller by a factor of 0.884 and f(s) is larger by a factor of 1.046. This agreement seems satisfactory for most purposes.

Similar results can be obtained for an exponential potential,

$$V(r) = \pm A \exp(-\alpha r), \tag{57}$$

where A and α are positive constants. The Massey-Mohr approximation for the phase shifts can be integrated exactly in terms of the modified Bessel function of the second kind,[26] but for most purposes the following asymptotic series[26,27] is satisfactory:

$$\delta(b) \approx \mp \left[\mu A/(\hbar^2 k)\right]\left[\pi b/(2\alpha)\right]^{\frac{1}{2}} \exp(-\alpha b)$$
$$\times\left[1 + (3/8)(\alpha b)^{-1} - (15/128)(\alpha b)^{-2} + \cdots\right]. \tag{58}$$

In this case the integrals for $S(0)$ and $\sigma(\theta)$ are best done by the Massey-Mohr random-phase approximation. The resulting expression for $S(0)$ as a function of v is parametric in b^*:

$$S(0) = 2\pi b^{*2}\left[1 + \tfrac{1}{2}(\alpha b^*)^{-1} + \cdots\right], \tag{59}$$

$$b^* \exp(-2\alpha b^*) = (\alpha/2\pi)(\hbar v/A)^2. \tag{60}$$

The expression for $\sigma(\theta)$ also involves the parameter b^*, but this can be eliminated in favor of $S(0)$ by iterative solution of (59), so that the result can be expressed in the same form as for the inverse power potential,

$$\sigma(\theta) = \left[kS(0)/4\pi\right]^2 G(\alpha) \exp\left[-g(\alpha)k^2 S(0)\theta^2/(8\pi)\right], \tag{61}$$

where

$$G(\alpha) = 1 + 8\pi\left[\alpha^2 S(0)\right]^{-1} + \cdots, \tag{62}$$

$$g(\alpha) = 1 + (2\pi)^{\frac{1}{2}}\left[\alpha^2 S(0)\right]^{-\frac{1}{2}} + \cdots. \tag{63}$$

Both $G(\alpha)$ and $g(\alpha)$ depend also on velocity implicitly through the velocity dependence of $S(0)$. Equations (59)-(61) are easily handled numerically by picking a series of arbitrary values of b^*, and for each one calculating the values of $S(0)$ and of $\sigma(\theta)$ from Eqs. (59) and (61), and then the corresponding value of v from Eq. (60).

C. Initial Quantum Deviations from the Classical Limit

We have indicated in Sec. IV A that the initial deviations from the classical limit are due to the use of the stationary phase approximation. Since it is difficult to calculate correction terms to the stationary phase approximation,[18,19] we do not expect to obtain much more from this approach than an indication of the angle and energy at which the quantum deviations begin to be important, and hence a more precise estimate of θ_c than the Massey-Mohr value of Eq. (1). Before presenting the results of this calculation, it is worthwhile to record the explicit results for the classical approximation. For the inverse power potential of Eq. (42), Kennard's small-angle formula (20) can be integrated to give[17]

$$\theta = \pm KC_s/(Eb^s), \tag{64}$$

where C_s is given by (44). This result can of course also be obtained by applying the relation $\theta = (2/k)(d\delta/db)$ to Eq. (43) for the phase shifts. From the general classical result that $S(\theta_o) = \pi\left[b(\theta_o)\right]^2$ we obtain

$$S(\theta_o) = \pi\left[KC_s/(E\theta_o)\right]^{2/s}, \tag{65}$$

and from the general classical relation of Eq. (30) we obtain

$$\sigma(\theta) = (1/s)(KC_s/E)^{2/s}(1/\theta)^{2+(2/s)} = b^2/(s\theta^2) = S(\theta)/(\pi s\theta^2). \tag{66}$$

If we take r_o in Eq.(1) for θ_c to be the distance of closest approach (or the impact parameter) for a classical scattering angle of θ_c, then substitution of (64) into (1) yields the explicit expression for θ_c,

$$\theta_c \approx \left[\pi^2\hbar^2/(2\mu)\right]^{s/(2s-2)} (KC_s)^{-1/(s-1)} E^{-(s-2)/(2s-2)} . \tag{67}$$

If we take $r_o = \left[S(0)/2\pi\right]^{\frac{1}{2}}$ as suggested by Massey and Mohr, and use the expression (45) for S(0), we obtain an expression exactly like (67), but multiplied by the factor

$$\left(\frac{s-1}{\pi^s}\right)^{1/(s-1)} \left[2\pi\Gamma\left(\frac{2}{s-1}\right) \sin\left(\frac{\pi}{s-1}\right)\right]^{\frac{1}{2}} . \tag{68}$$

This factor is unity for $s = \infty$, as might be expected, and is close to unity for finite s. For $s = 11$ it is 1.067, and for $s = 6$ it is 1.000. Even for $s = 3$ it falls only to $2/\pi = 0.637$.

Similar results hold for the exponential potential of Eq.(57). The Kennard small-angle formula (20) can be integrated exactly in terms of a modified Bessel function of the second kind,[28] but the following asymptotic series[28,29] is usually more convenient (first obtained by Amdur and Pearlman[30]):

$$\theta = \pm(A/E)(\pi\alpha b/2)^{\frac{1}{2}}\exp(-\alpha b)\left[1-(1/8)(\alpha b)^{-1}+(9/128)(\alpha b)^{-2}+ \cdots\right], \tag{69}$$

which can of course also be obtained by differentiation of Eq.(58) for the phase shifts. In principle, $S = \pi b^2$ could be found as an explicit function of θ by solving Eq.(69) for b, but it is much easier to leave S as an implicit function of θ and calculate it numerically by treating b as an arbitrary parameter, just as b^* was treated in connection with Eqs.(59)-(61). Similarly, it is easier to leave $\sigma(\theta)$ as an implicit function of θ. From Eqs.(30) and (69) the expression for $\sigma(\theta)$ is

$$\sigma(\theta) = \left[S(\theta)/\theta^2\right](\pi\alpha b)^{-1}\left[1+(1/2)(\alpha b)^{-1} + (3/8)(\alpha b)^{-2} + \cdots\right]. \quad (70)$$

We do not bother to write down the expression for θ_c for an exponential potential, since it is a transcendental equation whose form depends slightly on whether we take r_o as the classical distance of closest approach or use the Massey-Mohr value of $\left[S(0)/2\pi\right]^{\frac{1}{2}}$.

Although we have seen that the Massey-Mohr phase shifts yield the same final result in the classical limit as the Kennard small-angle formula, there is sometimes a real advantage to the direct use of the Kennard formula when it is applicable. The reason is that it is easy to improve the Kennard formula so that its range of accuracy extends to larger angles. All that is necessary is to use the distance of closest approach in place of b in Eqs.(20), (64), and (69) for θ, and then in the calculation of $S(\theta_o)$ and $\sigma(\theta)$ to use the classical relation,

$$b^2 = r_o^{\,2}\left[1 - V(r_o)/E\right], \quad (71)$$

where r_o is the distance of closest approach. The improvement in accuracy obtained in this way can be quite important in the analysis of experimental results.[29,31]

We now consider the corrections to the classical results. The general method of calculation by the stationary phase approximation has been given by Erdélyi,[19] and the application to molecular scattering problems is presented in detail elsewhere.[32] We therefore do not give details but only point out the special features for our particular case. In general, the major contribution (i.e., the classical limit) comes from the stationary point, and the quantum corrections may come from both the stationary point and the end points. Although the calculation can be carried through in complete generality for any arbitrary potential, for simplicity we restrict the discussion to potentials for which the phase shift δ_ℓ is a monatonic function of ℓ. Otherwise it is possible to have three (or more) stationary phase points corresponding to the three (or more) different classical impact parameters which produce the same absolute value of the scattering angle.[8,14] Although such behavior gives rise to a number of interesting physical phenomena,[14] we are here concerned only with the scattering at small angles, which corresponds to the outermost stationary point if three or more such points exist. For concreteness, we also assume that the phase shifts are negative, corresponding to a repulsive potential. The results are basically the same for small-angle scattering by an attractive potential, but the stationary point then occurs in the other integral.

The results can be summarized as follows.[32] There is no contribution to $f(\theta)$ from the end points at infinity. There is a small contribution from the end points at the origin, including an oscillating term, but these are of negligible magnitude in all cases considered here. The only contribution of importance thus comes from the stationary point, which gives a series for $f(\theta)$ in ascending powers of $\hbar^{1/2}$. The coefficients of the terms in $\hbar^{1/2}$, $\hbar^{3/2}$, etc., are identically zero, however, because the contributions to them from the two sides of the stationary point are equal and opposite. The remaining terms in integral powers of $\hbar$ are alternately real and imaginary, and so when the expression for $f(\theta)$ is squared to obtain $\sigma(\theta)$, the final series consists only of powers of $\hbar^2$. This result might well have been anticipated, because the quantum corrections to the transport cross sections occur[33] as a series in $\hbar^2$, and these cross sections are only weighted integrals of $\sigma(\theta)$ over all θ. The final result can be written in the form

$$\begin{aligned}\sigma(\theta)/\sigma_{c\ell}(\theta) = 1 + (2kb^2\theta')^{-2}\Big[&(b^4/6)(\theta^{V}/\theta') - (7b^4/6)(\theta^{IV}/\theta')(\theta''/\theta') \\ &- (2b^4/3)(\theta'''/\theta')^2 + (25b^4/6)(\theta'''/\theta')(\theta''/\theta')^2 - (5b^4/2)(\theta''/\theta')^4 \\ &+ (b^3/2)(\theta^{IV}/\theta') - (8b^3/3)(\theta'''/\theta')(\theta''/\theta') + (5b^3/2)(\theta''/\theta')^3 \\ &- (b^2/2)(\theta'''/\theta') + (3b^2/2)(\theta''/\theta')^2 + (3b/2)(\theta''/\theta') + 1\Big] + O(k^{-4}),\end{aligned} \tag{72}$$

where

$$\theta' = d\theta/db, \quad \theta'' = d^2\theta/db^2, \quad \theta''' = d^3\theta/db^3, \quad \text{etc.}, \tag{73}$$

and where $\sigma_{c\ell}(\theta)$ is given by Eq.(30). This result is not restricted to small angles if the potential is purely repulsive. For potentials with an attractive component, however, it is valid generally only for small angles.

For the inverse power potential, Eq.(72) becomes particularly simple in the small-angle limit:

$$\sigma(\theta)/\sigma_{c\ell}(\theta) = 1 + (2kb\theta)^{-2} + \cdots, \tag{74}$$

the next term being of order $(kb\theta)^{-4}$, and so on. It is remarkable that the parameter s of the potential has disappeared from the result. This correction term is of the same form as the correction for the higher terms of the asymptotic series for $P(b,\theta)$, as given in Eq.(40), although the correction term of Eq.(74) is numerically 16 times larger. An estimate of the magnitude of the correction term at the critical angle can be obtained by setting $\theta_c \approx \pi/(kb)$:

$$\sigma(\theta_c) \approx \sigma_{c\ell}(\theta_c)\left[1 + (2\pi)^{-2} + \cdots\right], \tag{75}$$

This correction is only about 2.5%, indicating that the classical results are accurate to angles less than θ_c, as is confirmed by the detailed numerical calculations in the next section. Integration of Eq.(74) yields the expression for the "total" cross section,

$$S(\theta_o)/S_{c\ell}(\theta_o) = 1 + (1/s)(2kb_o\theta_o)^{-2} + \cdots, \tag{76}$$

where $b_o \equiv b(\theta_o)$. The correction term is quite small, even for $\theta_o < \theta_c$.

Similar, but more complicated, expressions hold for the exponential potential.

D. Comparison with Experiment

As examples we consider the results for two high-energy systems, He-He and H-He, and one thermal energy system, K-Hg. We consider first the least favorable He-He case, which is Amdur and Harkness' measurement for a 500 ev He beam ($E = 250$ ev). The effective relative aperture of the apparatus was[2] 4.03×10^{-3} rad, and we calculate from Eq. (67) that the critical angle is 4.15×10^{-3} rad, using the parameters[2] $s = 5.94$ and $K = 7.55 \times 10^{-12}$ erg-Å^s. A plot of $\sigma(\theta)$ vs. θ is shown in Fig. 1 for this case. The small-angle quantum formula of Eq. (53) is drawn as a solid curve in its range of validity as given by Eq. (55), and then extended somewhat as a dashed curve. The almost classical formula of Eq. (74) is drawn down to about half the critical angle θ_c as a solid curve, and then extrapolated to somewhat smaller angles. The two formulas do not overlap, but they come sufficiently close that the rest of the curve could be interpolated with reasonable confidence. The figure shows that we can use Eq. (76) to obtain an estimate of the magnitude of the quantum deviations in Amdur and Harkness' results, and we find them to be less than 1%. For other energies and other apparatuses[30,34] the quantum deviations are still smaller. It is thus clear that the misgivings of Wu[1] are unjustified for He-He.

As a matter of fact, the disagreements between the quantum-mechanical calculations of V(r) and the V(r) calculated from the scattering measurements occur not for the measurements of Amdur and Harkness, but for measurements on apparatuses for which the quantum effects should be essentially negligible because of the larger values of θ_o. The Amdur-Harkness potential is really in fairly good agreement with quantum-mechanical calculations.[35]

As a check on our formulas, we can also calculate $\sigma(\theta)$ for He-He using an exponential potential with parameters[2] $\alpha = 4.55\text{Å}^{-1}$ and $A = 6.18 \times 10^{-10}$ erg. This potential was chosen by Amdur and Harkness to reproduce the inverse power scattering potential at small separations, and at large separations to join the He-He semiempirical potentials obtained from gas properties. The results are shown in Fig. 2, in which the exponential potential has been used to calculate the small-angle quantum result and the classical result, but not the almost classical result. Comparison with Fig.1 shows that the results for the two potentials are qualitatively similar, and are also in good quantitative agreement for $\theta>\theta_o$, which is the region investigated experimentally. Thus for the inverse power potential we calculate $S_{c\ell}(\theta_o) = 7.58\text{Å}^2$, and for the exponential potential we calculate $S_{c\ell}(\theta_o) = 7.74\text{Å}^2$, which differs by only 2.1%. The region for $\theta<\theta_o$ of course represents an extrapolation of the experiments, and here the two results differ by almost a factor of 2 as $\theta \to 0$. Only a very small part of this disagreement can be attributed to our mathematical approximations; most of it is due to the fact that the two potentials do not agree at the large separations corresponding to these small angles. The inverse power potential does not decrease rapidly enough with increasing r, and its extrapolation to large r predicts a much greater magnitude for V than does the similar extrapolation for the exponential potential. Consequently the small-angle scattering around $\theta = 0$ is consistently greater for the inverse power. However, the agreement of the two $\sigma(\theta)$ curves in the regions of θ corresponding to the regions of r where the two potentials agree shows that our mathematical results for the two forms of potential are in accord.

An even less favorable case than He-He has been mentioned by Amdur,[6] namely the H-He system.[36] At the lowest energy ($E = 350$ ev) we calculate from Eq. (67) that $\theta_c = 6.88 \times 10^{-3}$ rad, but the effective aperture in this case was only $\theta_o = 2.01 \times 10^{-3}$ rad. For this case the small-angle quantum results cannot be calculated from the inverse power potential obtained by Amdur and Mason, because the value of s is so low ($s = 3.29$, $K = 3.75 \times 10^{-12}$ erg-$\mathring{A}^s$) that some of our formulas diverge. We have to use the exponential potential for the quantum results, although we can still use the inverse power potential for the classical and almost classical results. We have obtained an exponential potential with parameters $\alpha = 1.97 \mathring{A}^{-1}$ and $A = 12.5$ ev by fitting both the inverse power scattering potential and the crossing point of the H-He and H^- - He potential curves, as determined from electron detachment data.[37] The resulting $\sigma(\theta)$ curves are shown in Fig.3. Since θ_o falls definitely in the small-angle quantum regime in this case, we cannot use Eq.(76) to estimate the magnitude of the quantum deviations for $S(\theta_o)$, but must resort to graphical or numerical integration. Using a planimeter, we find $S(\theta_o)/S_{c\ell}(\theta_o) = 0.90$. Since the internal consistency of the measured cross sections is no better than about 16%, as evidenced by agreement between results obtained with different detectors,[36] the quantum effects are thus only of marginal importance for this system. It might be noted, however, that allowance for the quantum corrections would improve the agreement between the experimental results for the two detectors.

As a final example we consider the small-angle scattering of a thermal beam of K atoms by Hg atoms. This scattering is caused by the long-range attractive London potential, which varies as r^{-6}. A number of cases of small-angle scattering by the London forces have been experimentally investigated by the group at Bonn,[9] and we have chosen K-Hg merely as a typical example. In earlier measurements, Pauly[38] found $S(0) = 2190\,\mathring{A}^2$ and calculated that $K = 96 \times 10^{-10}$ erg-$\mathring{A}^6$ using the Massey-Mohr formula given by Eq.(47). This therefore corresponds to a relative velocity of $\hbar v = 6.69 \times 10^{-23}$ erg-cm, or to a relative kinetic energy of 0.068 ev. At this velocity, the more accurate Eq.(46) gives $K = 81 \times 10^{-10}$ erg-$\mathring{A}^6$, which is the value we have used. The critical angle is then calculated to be 5.1×10^{-3} rad in relative coordinates. The calculated curves for $\sigma(\theta)$ are shown in Fig.4, and are seen to be qualitatively similar to the curves of Figs.1-3. The experimental results for this and similar systems do indeed show this behavior,[9] although they are not shown in the original papers as approaching the classical curve from above at large angles. However, the experimental results give only relative values of $\sigma(\theta)$, and so a simple vertical scale change would yield curves like Fig.4.

V. DISCUSSION

We have discussed four rather general results. The first two are comparatively minor: (1) the Massey-Mohr formula for the phase shifts corresponds in the semiclassical limit to the Kennard small-angle formula for the classical deflection angle; (2) at small angles the Schiff approximation is exactly the same as the semiclassical approximation.

The third result is more important: in the semiclassical approximation the differential cross section varies as $\exp(-c\theta^2)$ for small θ. A rough expression for c in terms of S(0) is given by Eq.(36), and accurate expressions for inverse power potentials and exponential potentials are given by Eqs.(53)-(54) and Eqs.(61)-(63), respectively.

The fourth result, derived in detail elsewhere,[32] is an expression for the first term of an asymptotic series for the initial deviations from the classical limit of $\sigma(\theta)$. This is given by Eq.(72) without any very special restrictions on the form of the potential, and is proportional to $\hbar^2$. Combined with the small-angle quantum formula of the preceding paragraph, this indicates that the accurate $\sigma(\theta)$ curve crosses the classical one and approaches it from <u>above</u> as θ increases, provided that any oscillating component is disregarded. Although the two formulas do not overlap without extrapolation, they are sufficiently close that the intermediate region can probably be covered by extrapolation for many cases of interest. In principle, the formulas could be extended somewhat in range, but the necessary calculations appear to be very laborious.

The present results indicate that the Massey-Mohr criterion for the critical angle θ_c is a reasonable one, but are more quantitative. In many cases the classical approximation may be reasonably accurate to angles considerably less than θ_c. Detailed calculations for He-He and H-He show that Wu's misgivings about Amdur's measurements are unjustified. To show that the detailed results are similar for low-energy (thermal) beams and long-range intermolecular forces, calculations for K-Hg have also been presented. It should be emphasized that these are valid only for small-angle scattering where the r^{-6} London potential is dominant; at large angles the repulsive parts of the potential are important and lead to several points of stationary phase, giving rise to such effects as orbiting, rainbows, and glories.[14] The rainbow effect has indeed been observed for K-Hg at large angles.[39]

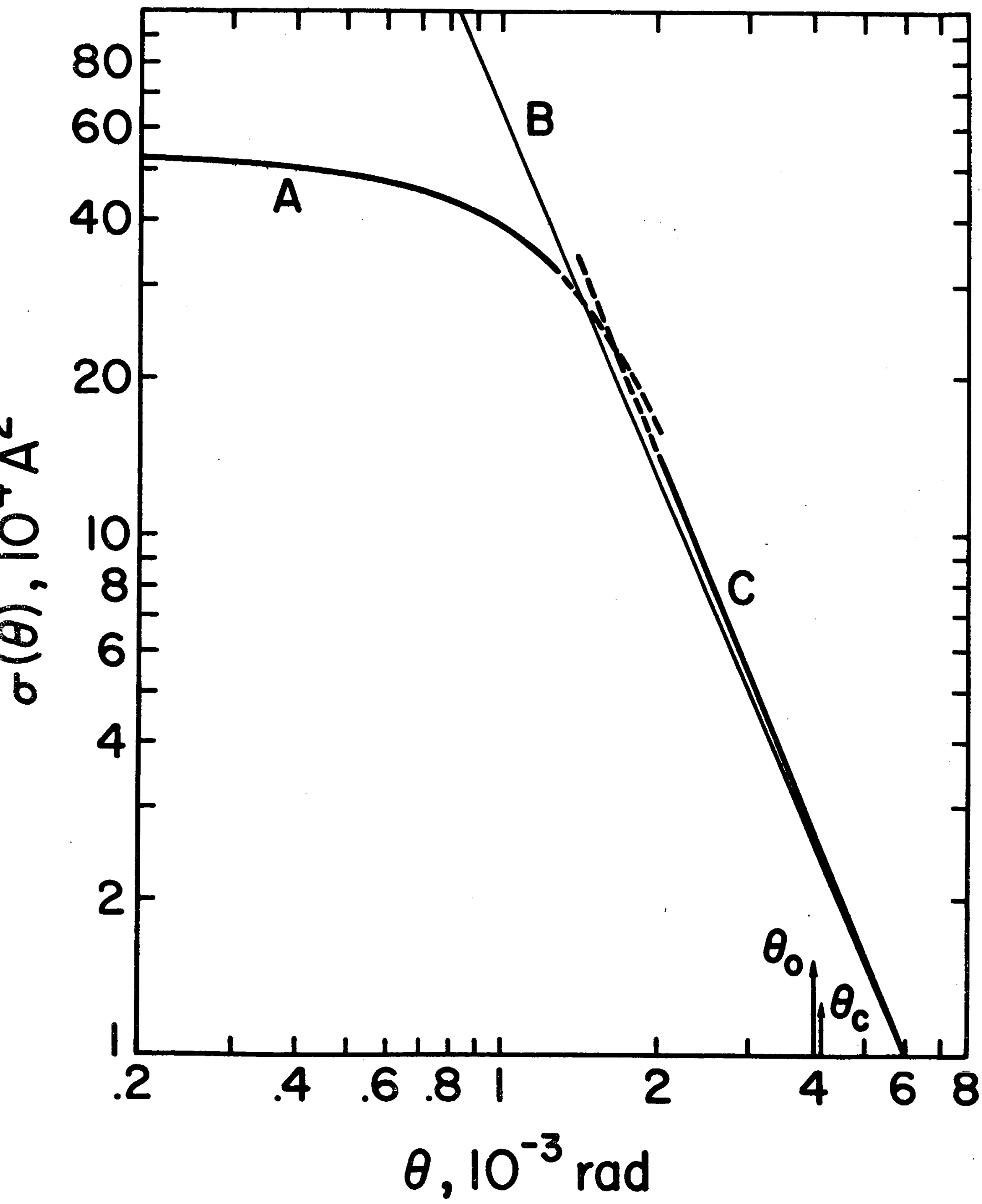
FIGURE CAPTIONS

Fig. 1 - Differential cross section for He-He at $E = 250$ ev, as calculated from an inverse power repulsive potential. Curve A is the small-angle quantum result according to Eq.(53), curve B is the classical result according to Eq.(66), and curve C the almost classical result according to Eq.(74).

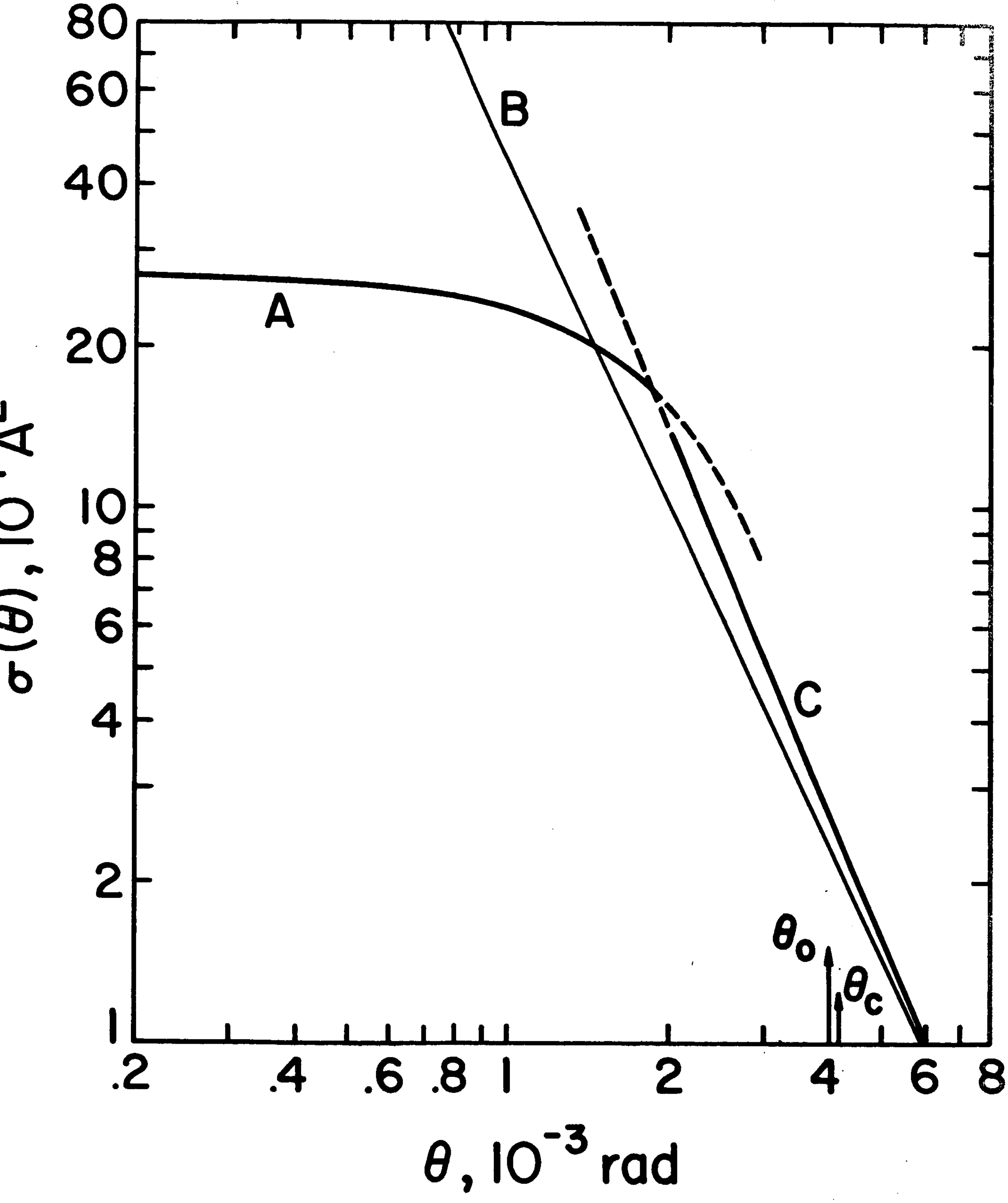
Fig. 2 - Same as Fig. 1, but calculated in part with an exponential repulsive potential. Curve A - quantum, Eq.(61); curve B - classical, Eqs.(69)-(70); curve C - almost classical, Eq.(74).

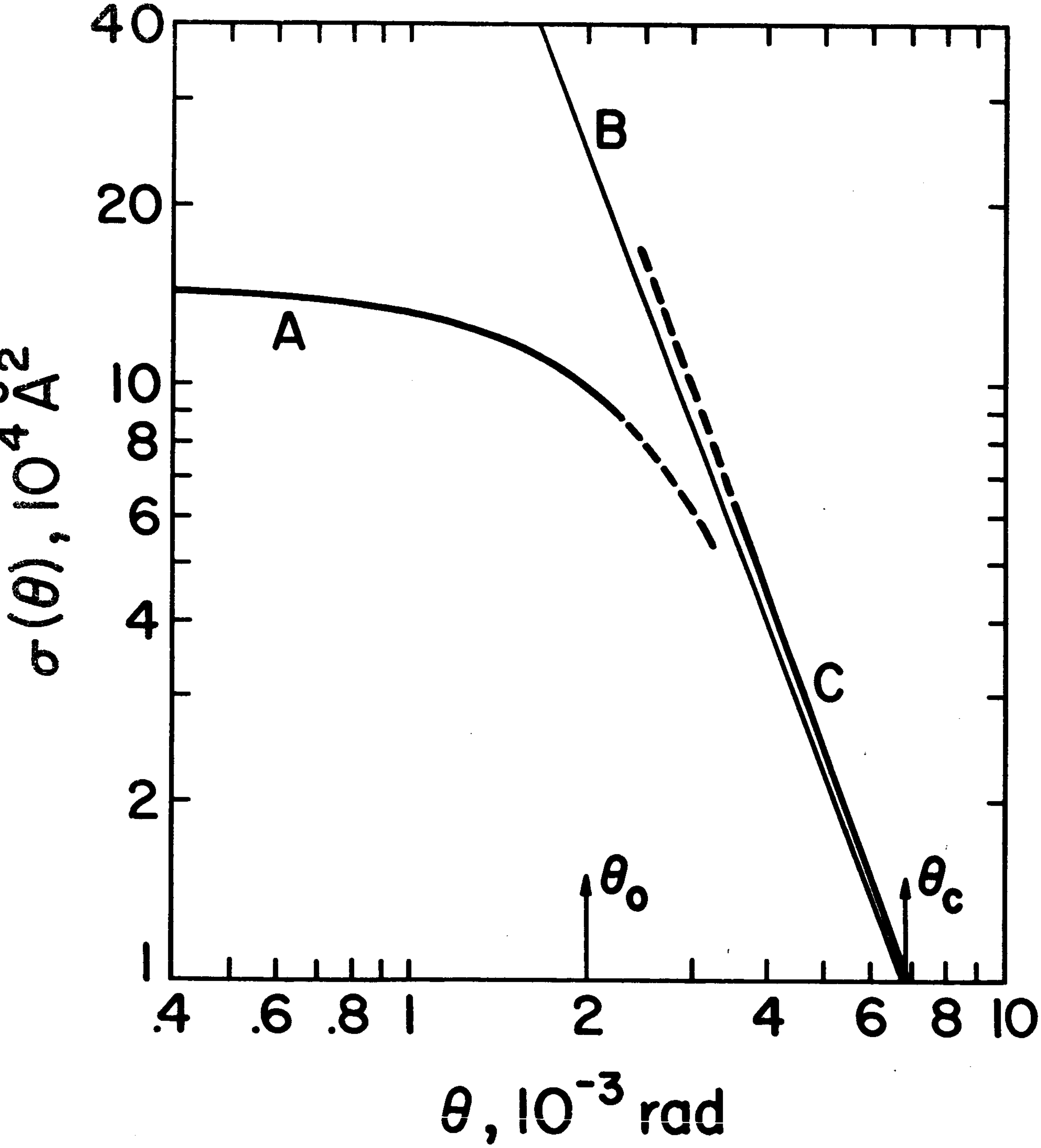
Fig. 3 - Differential cross section for H-He at $E = 350$ ev, as calculated from repulsive potentials. Curve A- quantum, Eq.(61); curve B - classical, Eq.(66); curve C - almost classical, Eq.(74).

Fig. 4 - Differential cross section for K-Hg at thermal energies, as calculated for an r^{-6} attractive potential. The labelling of the curves is exactly the same as in Fig. 1.

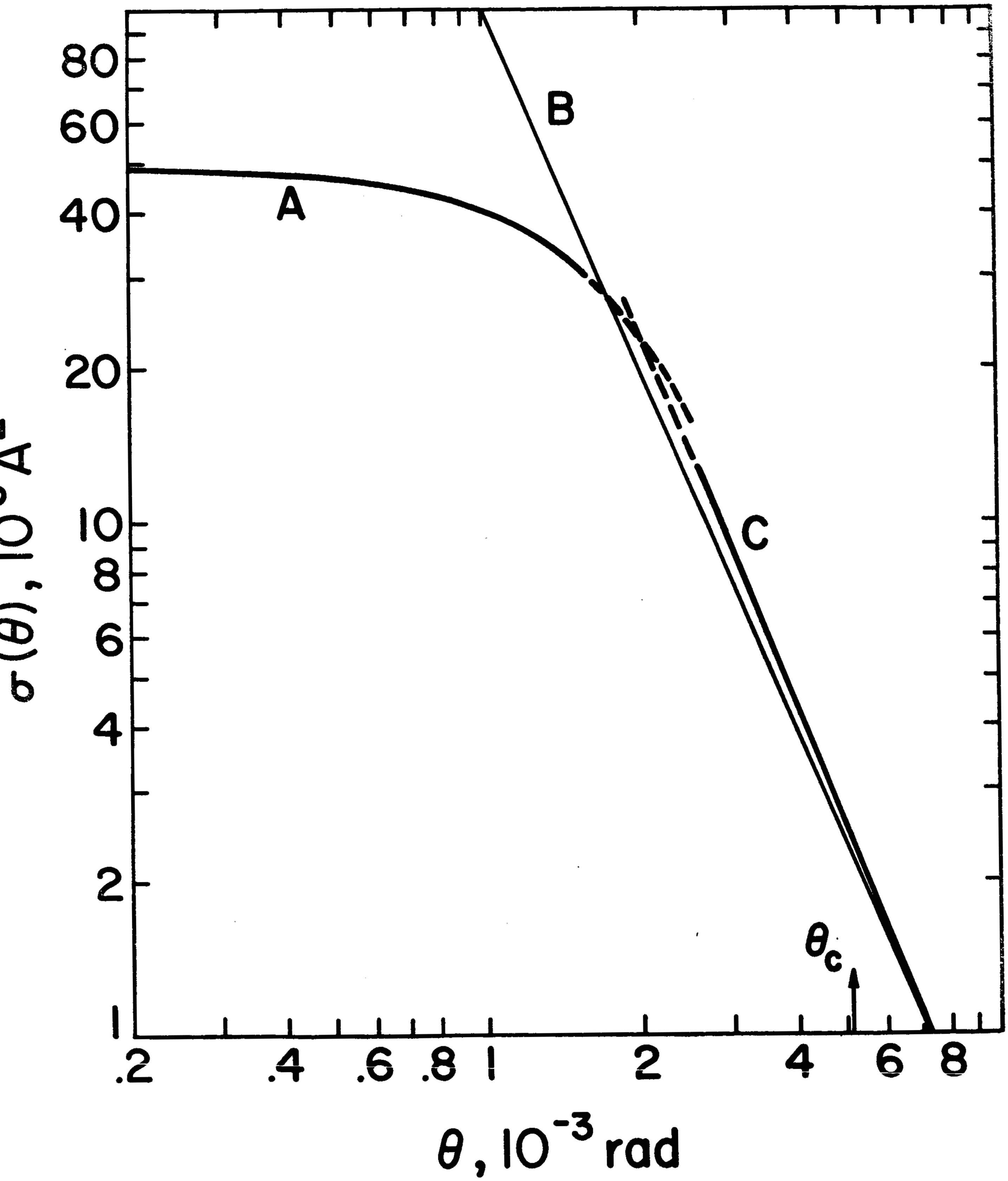


80
60
40
20
10
8
6
4
2
1
.2
.4
.6
.8
1
2
4
6
8
A
B
C
θ_o
θ_c
$\sigma(\theta)$, 10^4 Å^2
θ, 10^{-3} rad


80
60
40
20
10
8
6
4
2
1
σ(θ), 10⁴ Å²
A
B
C
θ₀
θ_c
.2
.4
.6
.8
1
2
4
6
8
θ, 10⁻³ rad



40
20
10
8
6
4
2
1
$\sigma(\theta)$, 10^4 Å^2
A
B
C
θ_o
θ_c
.4
.6
.8
1
2
4
6
8
10
θ, 10^{-3} rad



80
60
40
20
10
8
6
4
2
1
σ(θ), 10⁶ Å²
.2
.4
.6
.8
1
2
4
6
8
θ, 10⁻³ rad
A
B
C
θc

REFERENCES

1 T.-Y. Wu, J. Chem. Phys. 28, 986 (1958). See also T.-Y. Wu and T. Ohmura, Quantum Theory of Scattering (Prentice-Hall Inc., Englewood Cliffs, N.J., 1962), pp. 125-126.

2 I. Amdur and A. L. Harkness, J. Chem. Phys. 22, 664 (1954).

3 E. J. Williams, Revs. Modern Phys. 17, 217 (1945).

4 N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, London, 1949), Chap.7.

5 D. Bohm, Quantum Theory (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1951), pp. 528-529.

6 I. Amdur, J. Chem. Phys. 28, 987 (1958).

7 (a) H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A141, 434 (1933). (b) Ibid. A144, 188 (1934); here it is suggested that r_0 be taken as $r_0=[S(0)/2\pi]^{1/2}$, where S(0) is the quantum-mechanical total scattering cross section. This is very nearly the same as the classical distance of closest approach, as is shown in Sec.IV.

8 E. A. Mason, J. Chem. Phys. 26, 667 (1957). See also H. U. Hostettler and R. B. Bernstein, J. Chem. Phys. 31, 1422 (1959).

9 (a) H. Pauly, Z. Physik 157, 54 (1959). (b) Fortschr. Physik 9, 613 (1961).

10 Reference 4, Chap. 2.

11 L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1958), Chap.14.

12 An apparent exception is the high-energy He-He scattering,[2] in which struck recoil atoms might be expected to reach the detector. But in these experiments the angular aperture of the detector was so small that recoil atoms must have been struck nearly head-on in order to recoil into the detector,

and the kinetic energy of the beam atoms was so high that such collisions would probably cause ionization. Ions, however, were prevented from entering the detector chamber by an electric field.

13 L. I. Schiff, Phys. Rev. 103, 443 (1956).

14 K. W. Ford and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 259 (1959).

15 Reference 11, p. 167.

16 E. Jahnke and F. Emde, Tables of Functions (Dover Publications, Inc., New York, 4th edition 1945), p. 117.

17 E. H. Kennard, Kinetic Theory of Gases (McGraw-Hill Book Co., Inc., New York, 1938), pp. 119-120.

18 C. Eckart, Revs. Modern Phys. 20, 399 (1948).

19 A. Erdélyi, Asymptotic Expansions (Dover Publications, Inc., New York, 1956), pp. 51-56.

20 Reference 19, pp. 36-37.

21 R. P. Marchi and C. R. Mueller, J. Chem. Phys. 36, 1100 (1962), 38, 740 (1963); R. B. Bernstein, J. Chem. Phys. 36, 1403 (1962); similar results have also been obtained by L. Monchick (private communication).

22 J. B. Scarborough, Numerical Mathematical Analysis (The Johns Hopkins Press, Baltimore, Maryland, 1950), pp.156-157. See also J. E. Mayer and M. G. Mayer, Statistical Mechanics (John Wiley and Sons, Inc., New York, 1940), pp.152, 431-432.

23 R. B. Bernstein and K. H. Kramer, J. Chem. Phys. 38, 2507 (1963).

24 R. G. J. Fraser, H. S. W. Massey, and C. B. O. Mohr, Z. Physik 97, 740 (1935); see also K. F. Smith, Molecular Beams (Methuen and Co. Ltd., London, 1955), p.39.

25 E. T. Whittaker and G. N. Watson, Modern Analysis (Cambridge University Press, London, 4th edition 1927), p.260.

26 A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. (London) A69,615 (1956); M. R. C. McDowell, ibid. 72, 1087 (1958); A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. (London) A250,411 (1958).

27 E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 29, 361 (1958).

28 R. B. Bernstein, J. Chem. Phys. 38, 515 (1963).

29 E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 27, 917 (1957).

30 I. Amdur and H. Pearlman, J. Chem. Phys. 9, 503 (1941).

31 M. C. Kells, J. Chem. Phys. 16, 1174 (1948).

32 F. J. Smith, J. T. Vanderslice, and E. A. Mason, to be published.

33 J. de Boer and R. B. Bird, Phys. Rev. 83, 1259 (1951); Physica 20,185 (1954); S. I. Choi and J. Ross, J. Chem. Phys. 33, 1324 (1960).

34 I. Amdur, J. Chem. Phys. 17, 844 (1949); I. Amdur, J. E. Jordan, and S. O. Colgate, ibid. 34, 1525 (1961); I. Amdur and R. R. Bertrand, ibid. 36, 1078 (1962).

35 P. E. Phillipson, Phys. Rev. 125, 1981 (1962), and earlier papers referred to therein.

36 I. Amdur and E. A. Mason, J. Chem. Phys. 25, 630 (1956).

37 E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 28, 253,1070 (1958).

38 H. Pauly, Z. angew. Physik 9, 600 (1957).

39 F. A. Morse and R. B. Bernstein, J. Chem. Phys. 37, 2019 (1962).